soln. TLC was performed on Si gel HF_{254} (Merck, Type 60), and Si gel (Merck, 70–230 mesh) was used for column chromatography.

Isolation of the aglycone mixture. The tuber of *Solanum tuberosum* L. was harvested in early September 1975. At this time, they were separated into 3 groups according to diameter (*ca* 2, 5, and 8 cm). Treatment of epidermis of each tuber by the procedure described below gave a neutral compound. The remainder of the tubers were allowed to stand at room temp. for about 4 months in a dark room and the epidermis of just budding tuber was treated in the same manner. By the use of TLC, 4 samples were compared (colour producing reagent: $SbCl_3$). For extraction, the epidermis of just budding tuber and its bud were used. The dried material (2 kg) was extracted with MeOH by a Soxhlet apparatus until the extract became colourless. Evaporation of the solvent gave a brownish crude glycoside (97 g). It was hydrolyzed by refluxing in 2 l. of 1N HCl in MeOH for 6 hr, the hydrolysate was made alkaline with 5N NaOH and then extracted 3 × 400 ml portions of Et_2O. The alkaloidal fraction was removed with 5% tartaric acid solution (0.4 l × 3). The Et_2O phase was dried over Na_2SO_4 and evaporated to yield 6.9 g of neutral fraction.

Barogenin (3b). The neutral fraction was chromatographed over 210 g of Si gel and the column was eluted successively with C_6H_6, C_6H_6–Et_2O (19:1, 9:1, and 4:1), $CHCl_3$, and MeOH. The eluate with $CHCl_3$ and MeOH gave 80 mg of barogenin fraction. PLC (Si gel HF_{254}, 10% MeOH in $CHCl_3$) of the barogenin fraction and two recrystallizations of crude barogenin from Me_2CO gave needles (19 mg), mp 196–199°, $[\alpha]_D^{18}$ − 88.8° (*c*, 0.36 in $CHCl_3$). MS *m/e*: 412 (M^+-H_2O), 397 (M^+-H_2O-Me), 382 (M^+-H_2O-2Me), 115 (base peak). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400–3500, 1730, 1705. NMR (δ): 0.82 (3H, *s*, c-18), 0.96 (3H, *d*, *J* = 7 Hz, c-27), 1.05 (3H, *s*, c-19), 1.06 (3H, *d*, *J* = 7 Hz, c-21), 3.48 (2H, *d*, *J* = 6 Hz, c-26), 3.50 (1H, *m*, 3α-H), 5.37 (1H, *m*, c-6). (Calcd for $C_{27}H_{42}O_4$: C, 75.31; H, 9.83. Found: C, 75.24; H, 9.75%) Barogenin (18 mg) was acetylated in the usual manner and recrystallization of the product from MeOH gave 14 mg of barogenin acetate (**3b**-acetate), mp 136–137.5°. MS *m/e*: 454 (M^+-AcOH), 394 (M^+-2AcOH), 115 (base peak). NMR (δ): 0.83 (3H, *s*, c-18), 0.96 (3H, *d*, *J* = 7 Hz, c-27), 1.07 (3H, *s*, c-19), 1.07 (3H, *d*, *J* = 7 Hz, c-21), 2.03 (3H, *s*, O-Ac), 2.05 (3H, *s*, O-Ac), 3.94 (2H, *d*, *J* = 6 Hz, c-26), 4.60 (1H, *m*, 3α-H), 5.38 (1H, *m*, c-6). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735 (shoulder), 1730, 1705, 1260.

Conversion of barogenin acetate (3b-acetate) into yamogenin (**1b**). A mixture of 10 mg barogenin acetate, 5 ml MeOH, and 20 mg $NaBH_4$ was stirred at room temp. for 2 hr and the excess $NaBH_4$ was destroyed by dilute HCl. The mixture was extracted with $CHCl_3$ and worked up as usual. The solvent was evaporated to dryness and the residue was recrystallized from Me_2CO to give 3 mg of compound **1b**, mp 199–201°, MS *m/e*: 414 (M^+), 399, 396, 384, 139 (base peak). The identity of this compound with yamogenin (25*S*) was confirmed by IR, TLC [solvent system: EtOAc–cyclohexane (1:1)], GLC (column: 1.5% SE-30, column temp. 250°), MS, and mmp with authentic yamogenin (mp 200–201°, mmp 197–200°). IR ν_{max}^{Nujol} cm^{-1}: 3450, 1663, 1220, 1066, 996, 923, 900, 860.

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NEW ARBUTIN DERIVATIVES FROM LEAVES OF *GREVILLEA ROBUSTA* AND *HAKEA SALIGNA*

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Key Word Index—*Grevillea robusta*; *Hakea saligna*; Proteaceae; arbutin; 2-*p*-coumaroylarbutin; 6-*p*-coumaryl-arbutin; 6-caffeylarbutin; 6-*p*-hydroxybenzoylarbutin.

Previous work has shown the presence of 5 *n*-alkyl resorcinols [1], mono and bis norstriatols [2] in the wood and rutin, 2,5-dihydroxycinnamic acid, methyl 4-hydroxycinnamate, robustol and related macrocyclic phenolics [3] and arbutin in the leaves of *Grevillea robusta*. We felt that methyl 4-hydroxycinnamate might be an artifact produced by methanolysis during extraction and hence reinvestigated the leaves. From the acetone extracts, by extensive column and preparative TLC methods, arbutin and two new arbutin derivatives were separated. By the usual technique of permethylation studies and NMR analysis of their acetates, the last two were identified as 2-*p*-coumaryl- and 6-*p*-coumaryl-arbutins. Of these the former was in major amount. *p*-Hydroxybenzoyl-arbutin was absent.

The leaves of *Hakea saligna* were similarly examined and the combined acetone and methanol extracts yielded 2-*p*-coumaryl- and 6-caffeyl- and 6-*p*-hydroxybenzoyl-arbutins. The last was the major glycoside. No 6-*p*-coumarylarbutin was detected in the leaves. A comparison of the arbutin derivatives in the leaves of the two Proteaceae shows that *p*-hydroxybenzoylarbutin is restricted to *H. saligna* and 6-*p*-coumarylarbutin to *G. robusta*. Such differences may have taxonomic implications. Previously known arbutin derivatives from other sources are 2-*O*-gallyl- and 6-*O*-gallylarbutins, *p*-gallyl-arbutin (4) and 2-*O*-caffeylarbutin [5].

During a study of the NMR spectra of the acetates of the new glycosides, it was observed that all the protons of the cinnamyl moiety showed considerable upfield

shift if the acylation was at C_2 of sugar unit. All these protons absorbed upfield of the signal due to the aromatic protons of the hydroquinone ring. In the 6-acylated arbutins, except for the α-olefinic protons, all the other protons absorbed at lower fields than the quinol ring protons. The upfield shift obviously arises from the shielding from the aromatic ring of the hydroquinone moiety at C_1 of glucose. A study of molecular models of these arbutin derivatives shows that in both 2- and 6-cinnamylarbutins, such a shielding is possible. However the effect is observed only in acetylated 2-cinnamylarbutins and this would indicate some conformational preferences in these compounds.

EXPERIMENTAL

Air dried leaves of *Grevillea robusta* (500 gm) (collected from Delhi University Campus) were extracted exhaustively with C_6H_6, Me_2CO and CH_3OH respectively. Me_2CO extract was evaporated to dryness *in vacuo*; the residue was macerated with Et_2O to remove the soluble portion. The Et_2O insoluble portion was then dissolved in MeOH, and chromatographed (Si gel) affording: (i) 6-*O*-*p*-coumarylarbutin; from C_6H_6–EtOAc (3:2) eluates followed by PLC on Si gel in EtOAc (150 mg), mp 64–65°, $[\alpha]_D$ could not be measured. λ_{max}^{MeOH} 315 nm. ν_{max}^{KBr} 3420 br(OH), 1687 (—CO), 1600, 1580, 1508 (aromatic), 820 (1,4-substitution) cm^{-1}, deep blue fluorescence in UV light; *penta-acetate* with Py–Ac_2O in cold, crystallized from MeOH as colourless needles, mp 194–195°, $[\alpha]_D^{28.5}$ + 52.9° ($CHCl_3$; *c*, 0.46) (Found: C, 59.1; H, 5.3. $C_{31}H_{32}O_{14}$ requires C, 59.2; H, 5.09%), PMR δ 7.65 (*d*, *J* = 17 Hz, 1-H), 7.56 (*d*, *J* = 10 Hz, 2H), 7.12 (*d*, *J* = 10 Hz, 2H), 6.98 (*s*, 4H), 6.42 (*d*, *J* = 17 Hz, 1H), 4.34–5.28 (*m*, sugar protons), 2.29 (*s*, 1-OAc), 2.23 (*s*, 1-OAc), 2.04 (*s*, 3-OAc); ν_{max}^{KBr} 1750, 1712, 1500, 1370, 1210, 1154, 1050, 830 cm^{-1}. (ii) 2-*O*-*p*-Coumarylarbutin: from C_6H_6–EtOAc (1:1) eluates (1.5 g), mp 216–218°, $[\alpha]_D^{28}$ − 67.2° (MeOH; *c*, 0.59), λ_{max}^{MeOH} 275, 325 nm, ν_{max}^{KBr} 3400 br(OH), 1692 (—CO), 1600, 1610, 1504 (aromatic), 1290, 1260, 1210, 858, 825 cm^{-1}, *penta-acetate* with Py–Ac_2O in cold crystallized from MeOH, mp 138–139°, $[\alpha]_D^{28.5}$ + 4.2° ($CHCl_3$; *c*, 0.49) (Found: C, 59.9; H, 5.1. $C_{31}H_{32}O_{14}$ requires C, 59.2; H, 5.09%). PMR δ 6.97 (*s*, 4H), 6.81 (*d*, *J* = 10 Hz, 2H), 6.67 (*d*, *J* = 16 Hz, 1H), 6.30 (*d*, *J* = 10 Hz, 2H), 6.15 (*d*, *J* = 16 Hz, 1H), 4.28–5.24 (*m*, sugar protons); 2.28 (*s*, 1-OAc), 2.15 (*s*, 1-OAc), 2.03 (*s*, 3-OAc); ν_{max}^{KBr} 1750, 1718, 1664, 1610, 1498, 1370, 1210, 1185, 850 cm^{-1}. (iii) arbutin (100 mg), identified by direct comparison.

Permethylation and hydrolysis. (a) NaH dispersion in oil (50%, 10 mg) was added to a solution of the 6-*O*-*p*-coumarylarbutin (5 mg) in DMSO (2 ml) and the mixture was left overnight. The product was kept at 80° for 1 hr. After cooling MeI (1 ml) was added and the mixture poured into iced H_2O and extracted with $CHCl_3$. The permethyl glycoside from $CHCl_3$ was hydrolysed with Kiliani's mixture. The hydrolysate was examined for methylated sugars when 2,3,4-tri-*O*-methyl-D-glucopyranose (tetrazolium test − ve) [6] was identified by direct comparison with authentic sample by PC in *n*-BuOH–EtOH–H_2O (5:1:4). The permethylated aglycones were also identified as hydroquinone monomethyl ether and *p*-methoxycinnamic acid by direct comparison with authentic samples on TLC in C_6H_6–MeOH–MeCOOH (45:8:4) (R_f 0.63, 0.68 resp) (b) The 2-*O*-*p*-coumarylarbutin (5 mg) was subjected to permethylation as described above and the methylated sugar after Kiliani hydrolysis of the product was identified as 3,4,6-tri-*O*-methylglucopyranose (tetrazolium test + ve) [6]. Air dried leaves of *Hakea salignia* (800 g) (collected from Ooty) were extracted exhaustively with C_6H_6, Me_2CO and MeOH respectively. The Me_2CO and MeOH extracts, found to be similar (TLC), were mixed, evaporated to dryness *in vacuo* and the residue was macerated with petrol. The petrol insoluble fraction was then dissolved in MeOH, chromatographed (Si gel) to yield: 6-*O*-*p*-hydroxybenzoylarbutin from C_6H_6–EtOAc (9:11) fraction (2 gm), mp 226–227°, $[\alpha]_D^{28}$ − 126.9° (MeOH; *c*, 0.52); λ_{max}^{MeOH} 260 nm; ν_{max}^{KBr} 3356 br(OH), 1692 (—CO), 1600, 1555, 1534, 1445, 1440, 1266, 1205, 1066, 832 cm^{-1}, *penta-acetate* with Py–Ac_2O at room temp., crystallized from MeOH as colourless rods, mp 168–170°, $[\alpha]_D^{28.5}$ + 25.9° ($CHCl_3$; *c*, 0.47) (Found: C, 57.6; H, 5.1. $C_{29}H_{30}O_{14}$ requires C, 57.8; H, 4.98%). PMR δ 7.96 (*d*, *J* = 10 Hz, 2H), 7.12 (*d*, *J* = 10 Hz, 2H), 6.85 (*s*, 4H), 4.34–5.11 (*m*, sugar protons), 2.31 (*s*, 1-OAc), 2.25 (*s*, 1-OAc), 2.05 (*s*, 3-OAc); ν_{max}^{KBr} 1748, 1721, 1590, 1495, 1453, 1370, 1220, 1190, 820 cm^{-1}. 6-Caffeylarbutin from C_6H_6–EtOAc (2:3) followed by preparative TLC over Si gel in $CHCl_3$–MeOH–H_2O (33:13.5:1.8), (200 mg), λ_{max}^{MeOH} 282 nm; ν_{max}^{KBr} 3509 br(OH), 1695 (—CO), 1634, 1511, 1449, 1206, 855, 826 cm^{-1}, deep yellow fluorescence in UV light, *hexa-acetate* with Py–Ac_2O in the cold, mp 86–87°, $[\alpha]_D^{28.5}$ + 65.04° ($CHCl_3$; *c*, 0.24) (Found: C, 56.5; H, 5.5. $C_{33}H_{34}O_{16}.H_2O$ requires C, 56.3; H, 5.1%) PMR δ 7.77 (*d*, *J* = 17 Hz, 1H), 7.29 (*m*, 3H), 7.01 (*s*, 4H), 6.44 (*d*, *J* = 17 Hz, 1H), 4.36–5.28 (*m*, sugar protons), 2.31 (*s*, 3-OAc), 2.08 (*s*, 3-OAc); ν_{max}^{KBr} 1748, 1724, 1493, 1361, 1208, 1176, 906, 826 cm^{-1}. 2-*O*-*p*-coumarylarbutin, from C_6H_6–EtOAc (2:3) fraction followed by preparative TLC in $CHCl_3$–MeOH–H_2O (33:13.5:1.8) (250 mg), mp 216–18°, *penta acetate* with Py–Ac_2O in cold, PMR δ 6.97 (*s*, 4H), 6.80 (*d*, *J* = 10 Hz, 2H), 6.68 (*d*, *J* = 17 Hz, 1H), 6.32 (*d*, *J* = 10 Hz, 2H), 6.16 (*d*, *J* = 17 Hz, 1H), 4.31–5.23 (*m*, sugar protons), 2.30 (*s*, 1-OAc), 2.16 (*s*, 1-OAc), 2.01 (*s*, 3-OAc). It was identified as 2-*O*-*p*-coumarylarbutin by comparison with the compound (ii) obtained from *Grevillea robusta* leaves (co-TLC, co-IR). Arbutin (100 mg), identified by direct comparison.

Permethylation and hydrolysis. 6-*O*-*p*-hydroxybenzoylarbutin and 6-caffeylarbutin (5 mg each) were subjected to permethylation as described earlier and the methylated sugars after Kiliani hydrolysis of the products were identified as 2,3,4-tri-*O*-methyl-D-glucopyranose (tetrazolium test − ve) [6] in both the cases. The permethylated aglycones were identified as hydroquinone monomethyl ether and anisic acid in the former and hydroquinone monomethyl ether and dimethyl caffeic acid in the latter.

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